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(54) Process for the application of non-stick and heat-resistant coatings to aluminium sheets

(57) The following description sets forth a process for the application, by roll units, of a no-stick coating to one side and of a heat-resistant coating to the other side of aluminium sheets, said sheets being drawable after paints drying and baking.

EP 0 692 316 A1

Description

Field of the invention

The present invention relates to a process for the application of no-stick and heat-resistant coatings to aluminium sheets. In particular, the invention relates to a process consisting of the lapping of the aluminium surface, which is then coated with a no-stick paint layer on one side and with a heat-resistant paint layer on the other side, both paint layers being applied by roll units. The claimed process is particularly useful for the production of aluminium cookware provided with no-stick lining and heat-resistant coating.

The term "cookware" is used herein to mean pots and relevant lids, pans, baking pans, oven trays, toaster or oven racks, kitchen utensils, spatulas, mixing spoons, and all other utensils usually employed for food preparation and cooking.

State of the art

The use of no-stick cookware has extraordinarily increased during the last 30 years. Consequently, studies have been and are still being conducted to develop no-stick paint formulations and relevant methods of application to the pot and pan surface coming into contact with food.

With a view to overcoming the difficulty of sticking water paints based on PTFE to metal surfaces, several methods for the treatment of said surfaces before paint application, e.g. degreasing or pickling or sandblasting, have been studied. Furthermore, very many formulations based on PTFE combined with other components to be laid on the metal surface on a single application or with more coats, each preferably being of a different composition, have been developed.

For example, a particularly effective way of pickling an aluminium surface for no-stick paint application is disclosed in Italian patent No. 1,226,347 filed by the same Applicant.

A water paint without PTFE, containing a surfactant, finely divided silica particles, a polyethersulphone (PES) or polyamidoimide (PAI) for application to a degreased metal substrate and acting as a bridge with the successive PTFE-based paint layer is disclosed in US patents Nos. 5,049,437 and 5,079,073.

A method for the preparation of an aluminium sheet previously sandblasted and coated with three layers of PTFE-based paint is described in US patent No. 4,818,350. Said paints were found to be unfit for roll units.

In spite of the wealth of formulations and applicative methods disclosed in the prior art, there is an urgent need for improving the adhesion of PTFE-based no-stick coatings to metal substrates, using simple and high-yield techniques.

A process for the roll-unit application of a no-stick coating to metal sheets to be shaped into cookware for household use is disclosed in Italian patent No. 1,226,348 filed by the same Applicant. Roll-unit application offers several advantages over spraying: it does not disperse polluting aerosols in workroom environments and allows larger production volumes. Conversely, the coatings obtained show an inferior aspect, in particular as far as the outer surface gloss is concerned.

The Applicant, in EP application No. 0607934, discloses some water paints formulations based on PTFE, PPS and PAI that may be applied by roll units to aluminium sheets, simply degreased before their shaping into pots and pans, and providing gloss characteristics comparable with those obtained by spraying.

In the course of subsequent research, the Applicant has carefully examined all possible ways to treat aluminium surfaces before coating application, in particular:

- Heat treatment

This treatment consists of aluminium sheet annealing at a temperature of 450°C approx. The system removes any residual trace of oil from the rolling mill process, but is ineffective towards the salts and oxides, if any, occurring on the surface. It involves high power costs and the sheet cooling phase is a hindrance to plant productivity.

- Alkaline degreasing

The surface is treated at 30°C to 60°C with an anionic or non-ionic surfactant added with sodium hydroxide and sequestering agents. A considerable surface cleaning is obtained; however, traces of sodium hydroxide are left on the surface even after repeated washings with water. It raises the problem of liquid effluents disposal.

- Acid degreasing

The surface is treated at 30°C to 60°C with an anionic or non-ionic surfactant added with mineral acids and sequestering agents. The surface cleaning obtained is fairly good; however, salt residues are left on the surface even after repeated washings with water. It raises the problem of liquid effluents disposal.

- Degreasing with solvents

The surface is treated with chlorinated organic solvents. The system is ineffective towards mineral salts and raises problems of solvents treatment and recycle.

- Lapping

It consists of the mechanical removal of a thin surface layer by abrasion. It does not allow the obtainment of low surface texture, but its productivity is high.

Technical problem

As concerns the shaping of a painted aluminium disk, the paint layer must be so flexible as not to allow the formation of scalings and checkings during shaping and, at the same time, must be firmly fixed to the metal surface.

As concerns pots and pans, the outer and inner sides have different functions, the former being meant for coming into contact with the source of heat, necessary for food cooking, while the latter is meant for coming into contact with food. Therefore, the two sides of the aluminium disk to be shaped into cookware are painted with layers of paints of different chemical characteristics, but with analogous mechanical properties making them capable of withstanding, without any damage, the deformations caused by disk drawing, which is performed when both sides have been painted. Furthermore, the two coatings must get through all standard tests reproducing the pot duty conditions (dishwashing machine, hot-scratching, repeated use vs. colour maintenance).

Therefore, with a view to optimizing the performance, the treatment of the surfaces to be painted must fit in with the types of paints to be used, safeguarding, at the same time, the ease of operations and the productivity of the cookware production lines.

Detailed description of the invention

Subsequent research conducted by the Applicant provided evidence that high-quality cookware with no-stick linings and heat-resistant coatings may be obtained through a single mechanical process combining aluminium substrate preparation with the application of two different paint formulations, one for the outer and one for the inner side of the pot.

According to a basic feature of the present invention, the process for applying two different coatings - one heat-resistant and the other no-stick - to an aluminiun sheet comprises the following main steps:

a) lapping of both sides of the sheet to obtain a surface texture index number (Ra) between 0.7 μm and 1.1 μm;
b) roll-unit application of a first layer of water paint, no-stick type, to one sheet side;
c) drying of the paint layer at 30° to 50°C;
d) baking of the first dried paint layer at a temperature of 400°C to 430°C for a period of 2 to 5 minutes;
e) roll-unit application of a second layer of paint, heat-resistant type, to the other sheet side;
f) drying of the paint layer at 30°C to 50°C;
g) baking of the second dried paint layer at a temperature of 280°C to 320°C for a period of 2 to 10 minutes.

Texture is measured by profilometers. The measurements of the surface texture referred to herein were performed by a profilometer, Mod. RT 60, available from ALPA SM, Milan. The texture index number (Ra) is given by the ratio of the integral of the surface microcavities to the sheet portion length explored in a cross direction in respect of the direction of rolling.

Typical water paints useful for the formation of the first no-stick paint layer are as disclosed in the European patent application No. 94119007.6 filed on Dec. 2, 1994 by the Applicant, and consist of aqueous dispersions of PTFE, PPS and PAI mixtures, with a PAI content of 5% to 10% by wt. and a carbon black content of 10% to 15% by wt.

Considering that the best no-stick coatings are obtained with PTFE-based paints not containing other resins, in the preferred embodiments of the present invention the paint layer in contact with the aluminium surface is overlaid with another layer of paint based on PTFE, without mixing PTFE with PPS and PAI.

In fact, the investigations conducted provide evidence that the paint film in contact with the aluminium surface secures not only a coating with the adhesiveness and flexibility required by drawing, but also a perfect adhesion both to the aluminium surface and to the paint superficial layer, even if this contains PTFE only.

In a more preferred embodiment of the present invention, a first layer of paint containing PTFE and PPS in a ratio ranging between 35:65 and 55:45 w/w is applied, dried, and overlaid with a second layer of paint containing PTFE and PPS in a ratio ranging between 55:45 and 80:20 w/w so as to obtain a layer of intermediate characteristics (and therefore acting as a bridge) between those of the layer in contact with the aluminium disk and of the outer layer.

After application of each layer, the paint is air dried slowly to evaporate the water and solvents, if any, present therein. The paint may be applied on a single application or with more coats, repeating steps b) and c) as many times as desired. One or more water paint layers may also be applied as primers and then one or more layers as finish. Once all layers have been applied, the layer is baked.

The paints are applied to the aluminium sheet to be drawn in such amounts as to form coatings which, when dry, are 10 to 25 μm thick, each time providing a paint layer of 5 μm max.

Drying is carried out at a disk temperature of 30°C to 50°C, with an air stream at 120°C max., to no aftertack to the touch.

Typically, the paints that may be used for the formation of the second heat-resistant paint layer are as disclosed in the Italian patent No. 1,230,623 and Italian patent application MI91 A 001983 (open to public inspection), filed both by the Applicant; said paints are based on silicone polyesters, associated, if necessary, with immiscible silicone oils, to obtain a polychrome and particularly attractive surface finish.

After application, the paint is air dried slowly to evaporate the water and solvents, if any, present therein. The paint may be applied on a single application or with more coats.

Once all layers have been applied, the dried layer is baked.

The paints are applied to the aluminium sheet to be drawn in such amounts as to form coatings which, when dry, are 10 to 25 μm thick, each time providing a paint layer of 5 μm max.

As already mentioned, drying is carried out at a disk temperature of 30°C to 50°C, with an air stream at 120°C max., to no aftertack to the touch. The cookware obtained by drawing aluminium sheets after painting as per the process of this invention exhibits a coating as high in quality as that of analogous cookware painted by spraying, after moulding and sandblasting of the aluminium disk.

EXAMPLES 1 - 5

The various substances used in the examples are available under the following trademarks:

- Algoflon D 60®, from Montefluos S.p.A.: 60% by wt. PTFE aqueous dispersions.
- Rhodeftal 200®, from Rhône Poulenc: 30% by wt. PAI solutions in N-methylpyrrolidone. Prior to use, Rhodeftal 200® had been treated with dimethylethanolamine (DMEA) in a steatite ball mill for a period of 96 hours to make PAI soluble in water.
- Fortron X 0205/60®, from Hoechst: PPS in powder.
- Collacrat PU 85®, from BASF: thickener (ethoxylated urethane).
- Rhoplex AC 61®, from Rohm and Haas: 45% by wt. acrylic resin aqueous dispersion.
- Printex 85®, from Degussa: carbon black.
- Rhône Poulenc 10369 A®, from Rhône Poulenc: silicone oligomers.

Preparation of paints A to F

The compositions (%) of water paints A to F, which were subjected to the application tests described hereinafter, are reported in Table 1 below.

Table 1

Compositions (%) of water paints A to F						
Component	**A**	**B**	**C**	**D**	**E**	**F**
Algoflon D60®	15.2	19.6	15.2	15.2	15.1	23.9
Fortron X0205/60^{R}	13.1	11.4	13.1	13.1	13.1	9.7
Rhodeftal 200®	5.5	5.5	5.5	5.5	11.2	5.5
DMEA	0.7	0.7	0.7	0.6	1.3	0.7
Printex 85®	3.5	3.5	3.0	1.2	3.5	3.5
Antisettling a.*	3.2	3.2	3.2	3.2	3.2	3.2
Homogenizer**	2.0	2.0	2.0	1.9	3.9	2.0
Collacrat PU85®	6.7	6.7	6.7	6.7	6.7	6.7
Rhoplex AC61®	3.2	3.2	3.2	3.2	3.2	3.2
Others***	6.9	6.0	6.9	6.9	6.9	5.0
Water	40.0	38.2	40.5	42.5	31.9	36.6

* The terms "Antisettling a." indicates ethoxylated nonylphenol (antisettling additive)

** The term "Homogenizer" indicates ethylene glycol monomethyl ether (homogenizing additive)

*** The term "Others" indicates various chemical compounds (dispersing agents, surfactants) present in the formulations available under the aforementioned trademarks.

The solution of PAI in N-methylpyrrolidone was treated with dimethylethanolamine to solubilize same in water. Said treatment was carried out in a steatite ball mill for a period of 4 days. The clear to slightly opalescent solution obtained was used in paint formulation.

Also PSS, before being used in paint formulation, was milled in the presence of water in a steatite ball mill for a period of 72 hours to obtain a homogeneous dispersion including solid particles sized 8 µm max. Finally, water paints A to F were prepared by mixing the various components in the aforesaid amounts (in addition to the components pretreated as described above) in a steatite ball mill for a period of 72 to 96 hours. A perfect homogenization of the mixture and a lowering in the solid particle size below 8 µm were thus secured.

Paint application

The apparatus used for continuous application of water paints to aluminium disks to be shaped into cookware consisted of a lapping machine followed by two consecutive painting lines, each consisting of four roll units, each of the first three units being followed by a hot-air tunnel for painted disk drying and the fourth by a small heater for disks final drying and baking. Aluminium disks were caused to pass under the lapping machine twice, i.e. for the lapping of both sides, and were then placed on a conveyor belt and continuously transferred from one painting line to the other.

The first painting line applied the no-stick coating (inside the pot) while the second line applied the heat-resistant coating (outside the pot).

The conveyor belt speed was set to secure no aftertack to the touch of the painted disks after drying.

The disks painted with the aforesaid apparatus were made of aluminium sheet, type 1050 (99.5% aluminium), which had been lapped to a surface texture (Ra) of 1 µm.

The first and the second roll units were set to secure a paint layer to be 5 µm thick (after drying).

The air temperature in the first three tunnels was set to 70°C and the residence time of the painted disks in each tunnel was of 5 minutes. The temperature of the last heater was set to obtain a 5 minutes' disks baking at 420°C. The third roll unit was set to secure a paint layer 5 µm thick (after drying).

Several paintings of aluminium disks were carried out by the apparatus and according to the method described above. In particular, Examples 1 to 5 were obtained as follows: the first roll unit was fed with paints A to E, the second roll unit was fed in all cases with paint F, and the third roll unit was fed in all cases with paint A, but without PPS and PAI.

The operating parameters of the second painting line were the same as those of the first line, except that the last heater was set to obtain an 8 minutes' disks baking at 290°C. All roll units of the second painting line were fed with a silicone polyester paint having the following composition:

- 30% of thermoplastic polymer consisting of terephthalic acid (304.5 parts by wt.), isophthalic acid (304.5 parts), neopentyl glycol (192.5 parts), and 1,4-butanediol (329.8 parts), which was prepared as disclosed in the aforementioned patent application No. MI91 A 001983 (open to public inspection) (Ex. 2, p. 8);
- 70% of termosetting polymer consisting of trimethylolpropane (172 parts by wt.), isophthalic acid (107 parts), adipic acid (40.4 parts), ethylene glycol acetate (379.1 parts) , Rhône Poulenc 10369 A^R (355 parts), tetrabutyltitanate (0.7 parts), and n-butanol (20.2 parts), which was prepared as disclosed in the aforesaid patent application No. MI91 A 001983 (open to public inspection) (Ex. 4, p. 10).

Adhesion and peeling tests on no-stick coating

The aluminium disks as per Examples 1 to 5, obtained as described above, painted and drawn at different depths, were subjected to adhesion test as per ISO 1520 and to peeling test as per ISO 2409.

The results obtained are shown in Table 2.

Table 2

Adhesion and peeling tests on no-stick coatings of Examples 1 to 5

Drawing	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5
4.0 mm	no	no	no	**	no
peeling	(+)	(-)	(+)	--	(+)
4.5 mm	no	no	no	--	no
peeling	(+)	(-)	(+)	--	(+)
5.0 mm	no	no	no	--	no
peeling	(+)	(-)	(+)	--	(+)
5.5 mm	no	no	no	--	no
peeling	(+)	(-)	(+)	--	(+)
6.0 mm	no	no	no	--	no
peeling	(+)	(-)	(+)	--	(+)
6.5 mm	no	no	no	--	no
peeling	(+)	(-)	(+)	--	(+)
7.0 mm	no	no	no	--	yes
peeling	(+)	(-)	(+)	--	(+)
7.5 mm	no	no	no	--	yes
peeling	(+)	(-)	(+)	--	(+)
8.0 mm	no	no	no	--	yes
peeling	(+)	(-)	(+)	--	(+)

Remarks:
- Crackings and checkings, if any, on the surface of painted and drawn disks are observed.
- Peeling below 1 mm is considered positive (+); it is negative (-) in all other cases.
- ** Painted disks of Example 4 show evident blisterings on leaving the baking heater after the third roll unit; therefore, they have not been subjected to the various tests.

Bend test on heat-resistant coating

Painted aluminium disks of Examples 1 to 5, obtained as indicated above, were subjected to a bend test - a well known test to paints manufacturers - consisting in bending a sheet metal by 180°.

The sheet is repeatedly bent by 180°. The successive bendings are indicated by an increasing T-bend number: the first bending is given No. 0, the second No. 1, and so on. The lower the number of T-bends, the severer the stress withstood by the coating. The presence or the absence of microcheckings in the coating is observed at the external point of maximum bending.

In the aforesaid Examples 1 to 5, heat-resistant coatings get through this test with a T-bend value of 2 to 3.

After immersion of bent disks in water at 90°C for a period of 10 minutes, the coating showed only few microcheckings which might be observed through a 30X microscope. Therefore, the sample got through the test.

Claims

1. Process for applying two different coatings - one heat-resistant and the other no-stick - to an aluminiun sheet comprising the following main steps:

   a) lapping of both sides of the sheet to obtain a surface texture index number (Ra) between 0.7 µm and 1.1 µm;
   b) roll-unit application of a first layer of water paint, no-stick type, to one sheet side;
   c) drying of the paint layer at 30° to 50°C;
   d) baking of the first dried paint layer at a temperature of 400°C to 430°C for a period of 2 to 5 minutes;
   e) roll-unit application of a second layer of paint, heat-resistant type, to the other sheet side;
   f) drying of the paint layer at 30°C to 50°C;
   g) baking of the second dried paint layer at a temperature of 280°C to 320°C for a period of 2 to 10 minutes.

2. The process according to claim 1, wherein the water paints, no-stick type, used in the said step b) consist of aqueous dispersions of PTFE, PPS and PAI mixtures, with a PAI content of 5% to 10% by wt. and a carbon black content of 10% to 15% by wt.

3. The process according to claim 1, wherein the paints, heat-resistant type, used in the said step e) are silicone polyesters.

4. The process according to claim 1, wherein the said steps b) and c) are repeated several times before performing the said step d).

5. The process according to claim 1, wherein the said steps e) and f) are repeated several times before performing the said step g).

6. The process according to claim 1, wherein in the said steps b) and e) the paints are applied in such amounts as to form coatings which, when dry, are 10 to 25 µm thick, each time providing a paint layer of 5 µm max.

7. The process according to claim 1, wherein the air stream used for drying in the said steps c) and f) is at 120°C max.

8. The process according to claim 3, wherein the said silicone polyesters are associated with immiscible silicone oils to obtain a polychrome and particularly attractive surface finish.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 10 7199

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	FR,A,2 643 806 (SEB SA.) * page 4, line 3 - line 15 * ---	1,3	B05D7/16 B05D5/08
A	WO,A,94 12346 (MITSUBISHI KASEI AMERICA INC.) * examples * ---	1	
A	EP,A,0 352 711 (NKK CORP.) * claims * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B05D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	6 July 1995	Brothier, J-A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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